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Aging of Class 1E Batteries in Safety Systems of Nuclear Power Plants

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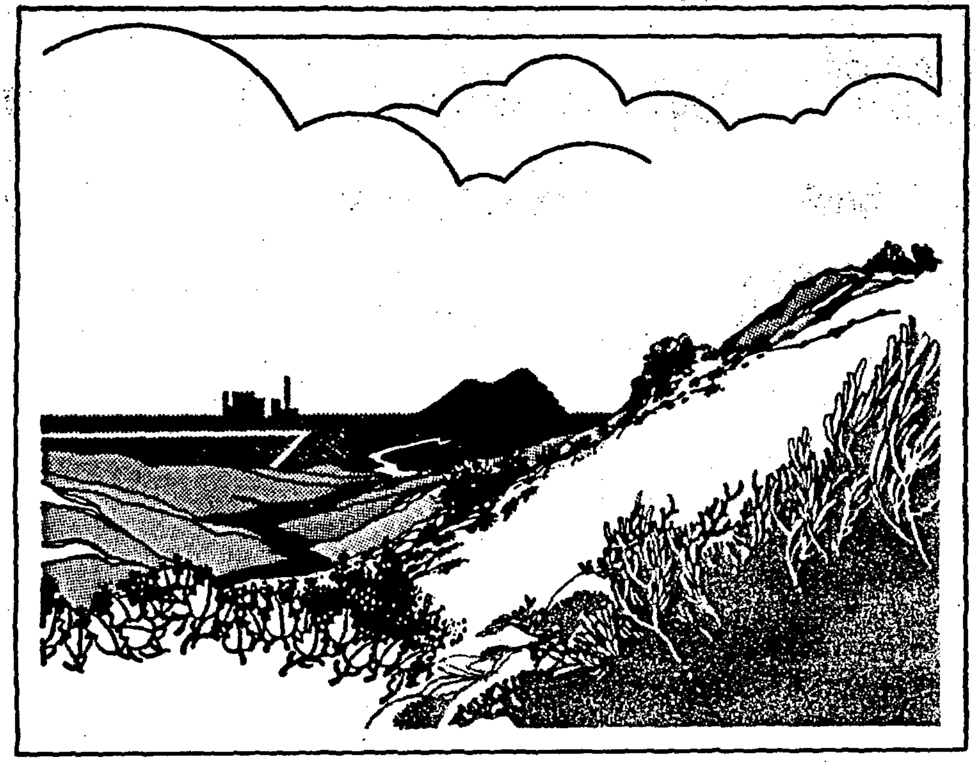
FORMAL REPORT



EG&G Idaho

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AGING OF CLASS 1E BATTERIES IN SAFETY SYSTEMS OF NUCLEAR POWER PLANTS

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ABSTRACT

This report presents the results of a study of aging effects on safety-related batteries in nuclear power plants. The purpose is to evaluate the aging effects caused by operation within a nuclear facility and to evaluate maintenance, testing, and monitoring practices with respect to their effectiveness in detecting and mitigating the effects of aging. The study follows the U.S. Nuclear Regulatory Commission's (NRC's) Nuclear Plant-Aging Research approach and investigates the materials used in battery construction, identifies stressors and aging mechanisms, presents operating and testing experience with aging effects, analyzes battery-failure events reported in various data bases, and evaluates recommended maintenance practices. Data bases that were analyzed included the NRC's Licensee Event Report system, the Institute for Nuclear Power Operations' Nuclear Plant Reliability Data System, the Oak Ridge National Laboratory's In-Plant Reliability Data System, and The S. M. Stoller Corporation's Nuclear Power Experience data base.

FIN No. A-6389—Aging/Systems Interaction Study:
Component Residual Lifetime Evaluation and Feasibility of Relicensing

EXECUTIVE SUMMARY

Batteries are installed at nuclear facilities to provide power to critical functions in the event of loss of all ac power. The batteries normally are floated (Floating is the term applied to the method of operation when the battery is continually connected to a battery charger to keep it in a fully charged condition by reason of the small amount of charging current that it receives.) by a battery charger that also supplies power for all the dc loads until the loss of ac power. The batteries then carry the dc loads. When this happens, batteries provide power for equipment vital to safe shutdown, control, and monitoring of plant parameters. Redundant batteries are installed to ensure that at least one safety train of accident-mitigating equipment is available given an assumed non-mechanistic single active failure in any safety system, including the Class 1E dc power system. Therefore, reliable operation of the batteries is necessary to ensure safety of a nuclear facility.

This report describes a study that was sponsored by the U.S. Nuclear Regulatory Commission's (NRC's) Office of Nuclear Regulatory Research (RES) and performed at the Idaho National Engineering Laboratory to evaluate aging effects on safety-related batteries in nuclear power plants. The study identifies materials used in battery construction, stressors and aging mechanisms, presents operating and testing experience, analyzes battery-failure events reported in various data bases, and evaluates recommended maintenance practices.

Data bases included the NRC's Licensee Event Report (LER) system, the Institute for Nuclear Power Operations' Nuclear Plant Reliability Data System (NPRDS), the Oak Ridge National Laboratory's In-Plant Reliability Data System (IPRDS), and The S. M. Stoller Corporation's Nuclear Power Experience (NPE) data base. The LER review covered about 20 years of data and events were classified by failure cause. The NPRDS review covered about 13 years of data and events were classified by failure cause and service age of the batteries. The IPRDS data from five nuclear plants has been reported by ORNL and were utilized for this study. Events were classified by failure mode. The NPE review covered about 25 years of data that is available in the public domain. Events were classified by failure cause.

Results of the evaluation of stressors indicate that the single most important aging-related stress mechanism for batteries is thermally induced oxidation of the grids and top conductors that are usually made of a lead-calcium alloy. Oxidation of the grids causes the plates (including grids) to swell, causing poor contact between the grid and the active material in the plate, and results in decreased capacity of the battery. Plate growth ultimately results in stressing the container and covers, causing cracks to develop in the container, and subsequent loss of electrolyte.

Evaluation of operating experience combined with testing of naturally aged batteries shows that cracking of the containers and oxidation (flaking) of the lead are significant problems. Seismic testing of five models of naturally aged batteries has identified oxidation of the lead, deterioration of separators, and cracking of containers as problems with batteries. These problems occur more frequently in old batteries near their end of life. Test results reported by Sandia National Laboratories have shown that degraded batteries are more susceptible to vibration and NRC Information Notices have suggested that a seismic event could produce a failure of old batteries. However, newer batteries qualified to the requirements of the Institute of Electrical and Electronic Engineer's (IEEE's) Std 535-1986, "IEEE Standard for Qualification of Class 1E Lead Storage Batteries for Nuclear Power Generating Stations," may be less vulnerable to seismic events because the IEEE standard requires seismic qualification with batteries aged to end-of-life conditions.

Analysis of the data bases has shown that events classified as representing a degraded or incipient failure condition are the most commonly reported failures. These events include low specific gravity, insufficient charge, cracked containers, corrosion, defective or weak cells, and faulty connections. Low specific gravity is the most common of these abnormal conditions, representing about 27% of the total battery-related events reported in LERs. Personnel errors in performing operations, maintenance, and testing also emerged as a significant factor, representing about 21% of the total battery-related events reported in LERs. Analysis of the NPRDS data base indicates that total battery failures peak 6 to 11 years after the batteries are placed into service. These appear to be age-related failures that are usually related to plate growth, deterioration of internal components, and cracked containers.

Evaluation of maintenance practices has shown that considerable care and attention to detail is required to maintain batteries operable and maintenance performed correctly leads to the long use of batteries. Further, batteries maintained in accordance with recommended practices in Regulatory Guide 1.129 and IEEE Std 450-1980 should be expected to provide reliable service for their qualified life. However, surveillance tests for identifying incipient seismic vulnerability of old batteries (other than seismic testing of selected cells) have not been identified. Because the useful electrical life of a battery is probably longer than its seismic-qualified life, old batteries not seismically qualified to end-of-life conditions could be operating with an undetected vulnerability to a seismic event.

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AGING OF CLASS 1E BATTERIES IN SAFETY SYSTEMS OF NUCLEAR POWER PLANTS

1. INTRODUCTION

The U.S. Nuclear Regulatory Commission (NRC) initiated the Nuclear Plant-Aging Research (NPAR) Program to obtain a better understanding of how degradation due to aging of key components could affect nuclear plant safety, if not detected before loss of functional capability; and how the aging process may change the likelihood of component failures in systems that mitigate transients and accidents. The possibility of aging degradation causing such events is also a concern.

This report presents an in-depth engineering study of batteries used in safety-related applications. The work supports the NPAR goals as stated in NUREG-1144[1], which are to:

- Identify and characterize aging and service-wear effects associated with electrical and mechanical components, interfaces, and systems likely to impair plant safety
- Identify and recommend methods of inspection, surveillance, and condition monitoring of electrical and mechanical components and systems that will be effective in detecting significant aging effects before loss of safety function so that timely maintenance and repair or replacement can be implemented
- Identify and recommend acceptable maintenance practices that can be undertaken to mitigate the effects of aging and to diminish the rate and extent of degradation caused by aging and service wear.

The NPAR Program is being conducted at several national laboratories including the Idaho National Engineering Laboratory (INEL). Other work at the INEL related to this battery-aging study includes the root cause studies of component failures for selected systems.[2,3] The root cause work identifies systems and components affected by aging, which included batteries, and calculates contributions to plant safety and system unavailabilities. Batteries are important components in the dc power systems, a subsystem of the Class 1E electrical distribution system.

This study addresses the materials susceptible to aging associated with batteries. Specific components, such as plates, cases, electrolyte, straps, and terminals have been studied extensively by other laboratories, with particular emphasis on component aging and seismic vulnerability.[4] These results are summarized in this report. Operating experience from generic data bases compliments the test results obtained by the other laboratories. Information sources used include: The NRC's Licensee Event Report (LER) system, the Institute for Power Reactor Operations' Nuclear Plant Reliability Data System (NPRDS), the Oak Ridge National Laboratory's In-Plant Reliability Data System (IPRDS), and The S. M. Stoller Corporation's Nuclear Power Experience (NPE) data base. Reports published by others who have studied battery failures caused by aging, texts describing battery materials and their susceptibility to aging, and standards and guides related to battery qualification and maintenance were also used to complete this overview.

Figure 1 shows the overall strategy of the NPAR Program and identifies the areas covered by this report. This report addresses Phase 1 of the NPAR Program and presents information pertaining to the type, uses, and description of batteries used in nuclear plants. This is followed by a discussion of materials used in battery construction and an identification of those materials most susceptible to aging. Next, significant stressors and aging mechanisms of batteries are identified, followed by a review of pertinent operating experience and results of testing performed by other laboratories. This is followed by an evaluation of battery-failure events reported in generic data bases. An interim assessment of existing maintenance, testing, and monitoring techniques is then performed, followed by a discussion of potential improved monitoring methods for detecting degradation leading to seismic vulnerability. Conclusions reached during the study are presented in the final section.

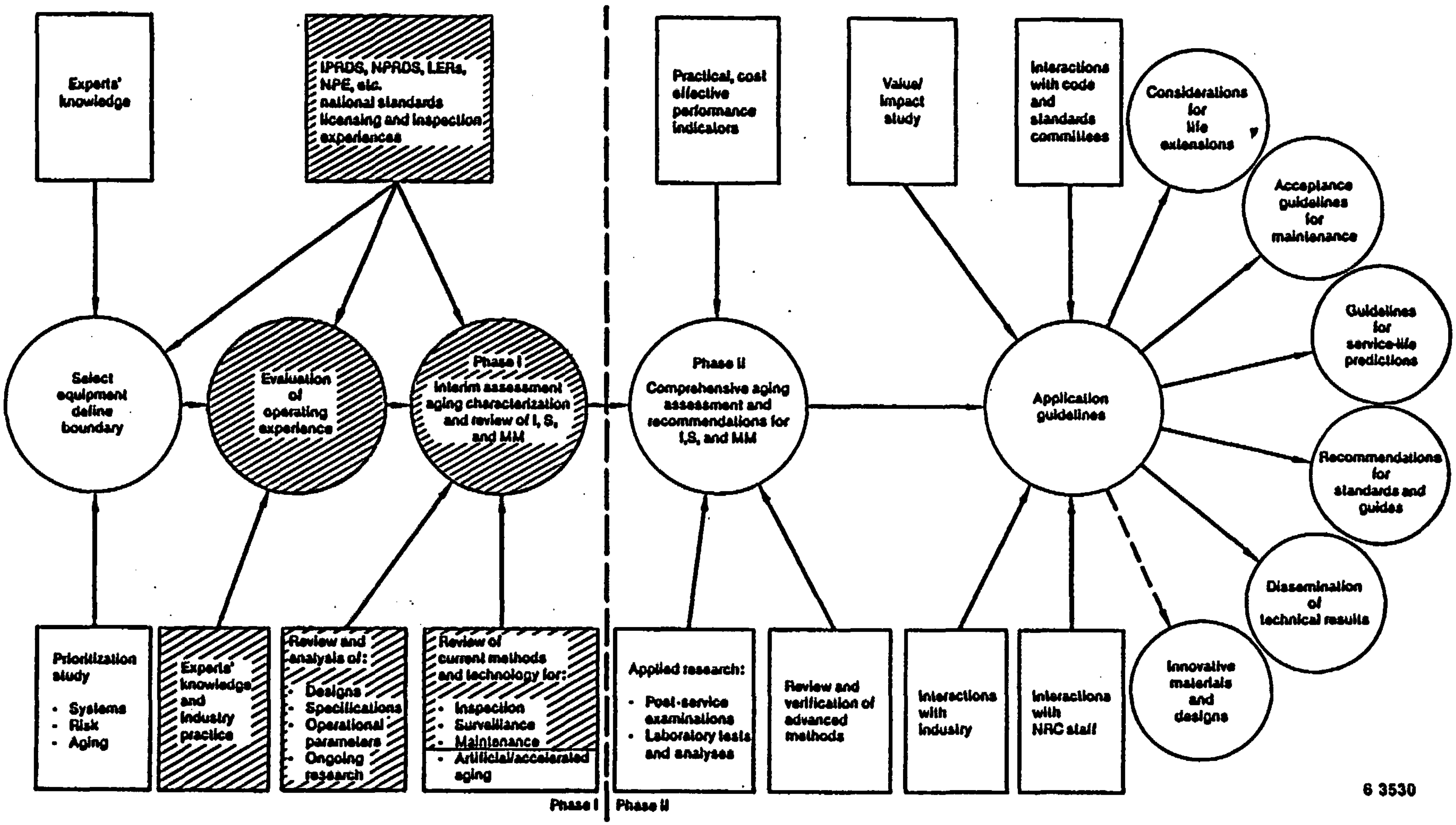

Figure 1. NPAR program strategy.

2. TYPE, APPLICATIONS, AND DESCRIPTION OF BATTERIES IN NUCLEAR POWER PLANTS

2.1 Identification of Battery Type and Applications

The batteries used in safety-related applications in nuclear power plants are lead-acid storage batteries and most are of the same basic design, flat plates with lead-calcium grids. Lead-antimony cells, as well as some other such as Ni-Cd, are being utilized in only a few (less than 10%) nuclear plants and, therefore, will not be addressed in this report. In the event of a loss of all ac power, batteries normally provide control power for starting diesel generators, operating electrical circuit breakers, and control of logic circuits associated with electrical safety equipment. Batteries also provide ac power through dc-to-ac inverters to the safety instrument buses. Some plants also use these batteries to control the switchyard circuit breakers when ac power is lost.[5] In the event of a station blackout (all offsite power is lost and the diesel generators do not start), the batteries are the only installed source of electrical power to provide for the safe shutdown of the nuclear reactor. Figure 2 is a diagram showing the various ac and dc components within a typical nuclear plant. A battery charger provides a float charge for the batteries and also supplies power for all the dc loads until the loss of emergency bus ac power; the batteries then carry the dc loads.

2.2 General Description

Batteries for Class 1E applications at nuclear power plants are typically composed of many (60 for a 125 V dc system) individual lead-acid storage cells that are connected together to provide the needed voltage and current for emergency situations. These cells, then, are the fundamental unit of the battery.[6] The essential parts of the cell are two dissimilar electrodes immersed in an electrolyte in a suitable container. The two dissimilar electrodes are composed of active material contained within a grid structure (usually referred to as a plate). The active material on both electrodes chemically combine with the electrolyte to provide the current during discharge, with the chemical reaction being reversed when the cell is being charged. The double-sulfate reaction of the lead-acid battery is most conveniently stated by the following reaction:

At positive plate:

$$PbO_2 + H_2SO_4 \rightleftarrows PbSO_4 + H_2O + O$$

At negative plate:

$$Pb + H_2SO_4 \rightleftarrows PbSO_4 + 2H$$

The combined reactions at the positive and negative plates are:

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O$$

The equations should be read from left to right for discharge and from right to left for charge. These equations represent the chemical reactions that take place under normal conditions. If impurities are present, other reactions will occur.[7]

It is important to note that the components of the reaction are insoluble in the electrolyte. Thus, under normal operating conditions the active materials remain in their respective positions.

The grid of a cell has two functions: first, as a support for the active material, which is not normally self supporting; and, second, as a conductor to transmit current from all parts of the active material to the plate terminal. Figure 3 shows a typical grid assembly. The plates are fused to conductors (straps) and posts at the top of the cell that transmit current from the plates to external connections to the cell. Figure 4 shows a typical post, strap, and seal assembly. Note the slots in the strap where plates are fused in the final battery assembly. Positive plates typically hang from the positive plate straps, container side walls, or are cantilevered from the negative plates to allow for positive plate growth. The negative plates are usually supported by the negative plate straps and by feet that rest on the floor of the battery case. The plates in batteries at nuclear plants are typically 15 in. high and 12.5 in. wide.

Plates are primarily of two basic designs, one called Planté (or formed) and the other referred to as Faure (or pasted). In the Planté type, the active material consists of a comparatively thin layer superficially formed from the metallic lead of the grid by an electrochemical process. This type of grid is found in some older batteries, but is not now commonly manufactured in the U.S. In the Faure type, the lead-oxide (PbO) active material is applied to the supporting grids in the form of a paste consisting of lead powder mixed with a liquid (water, dilute sulfuric acid, or other aqueous solution) to a putty-like consistency, followed by setting and drying. The plates are then formed by immersing them in dilute sulfuric acid and passing current through

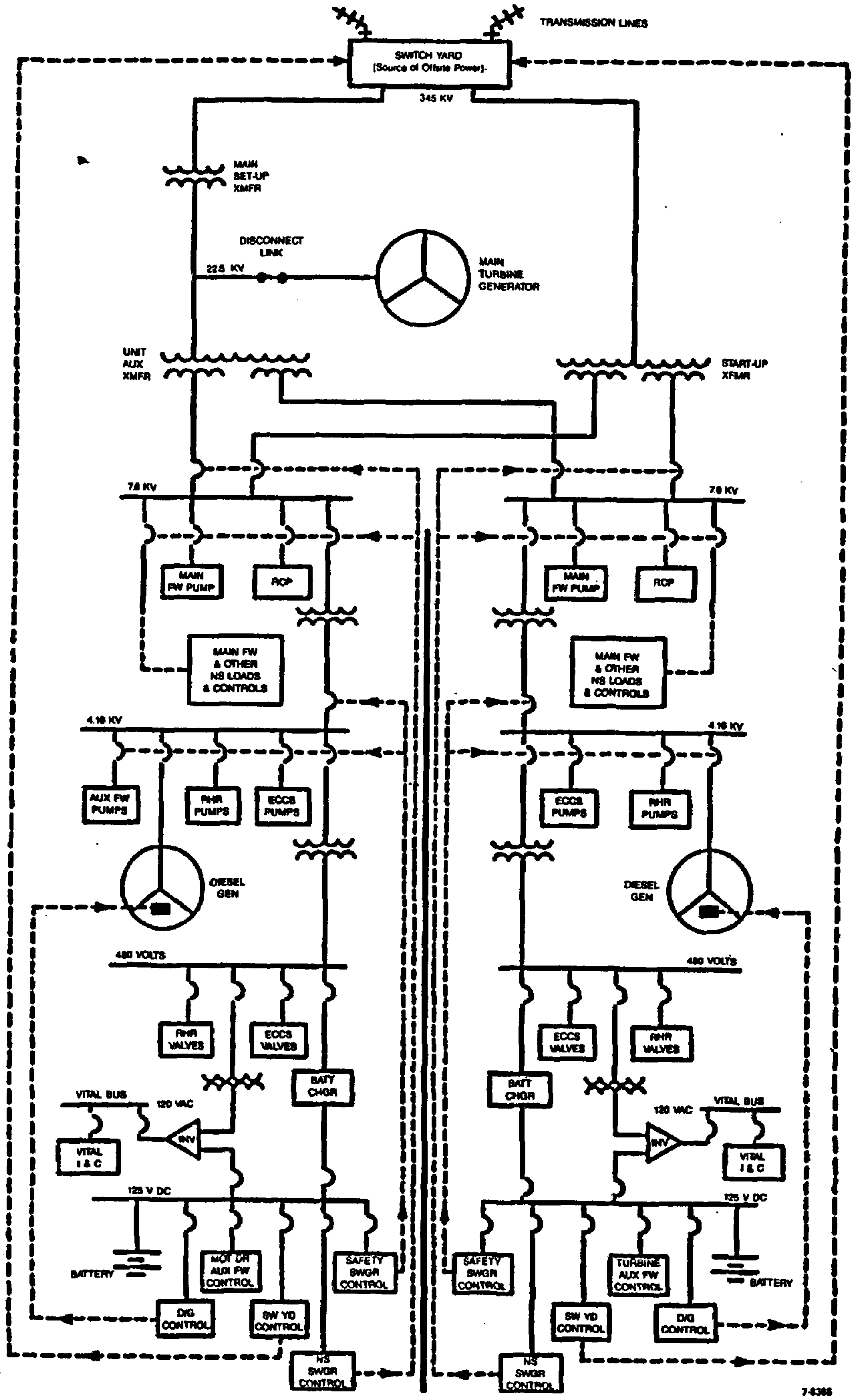

Figure 2. Typical PWR two division safety system—electrical line diagram.

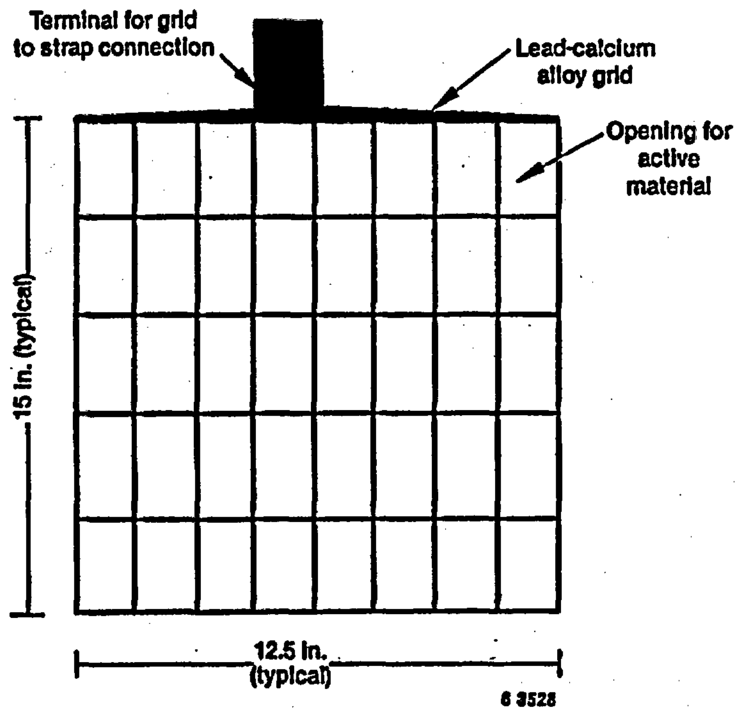

Figure 3. Typical grid of a pasted battery plate.

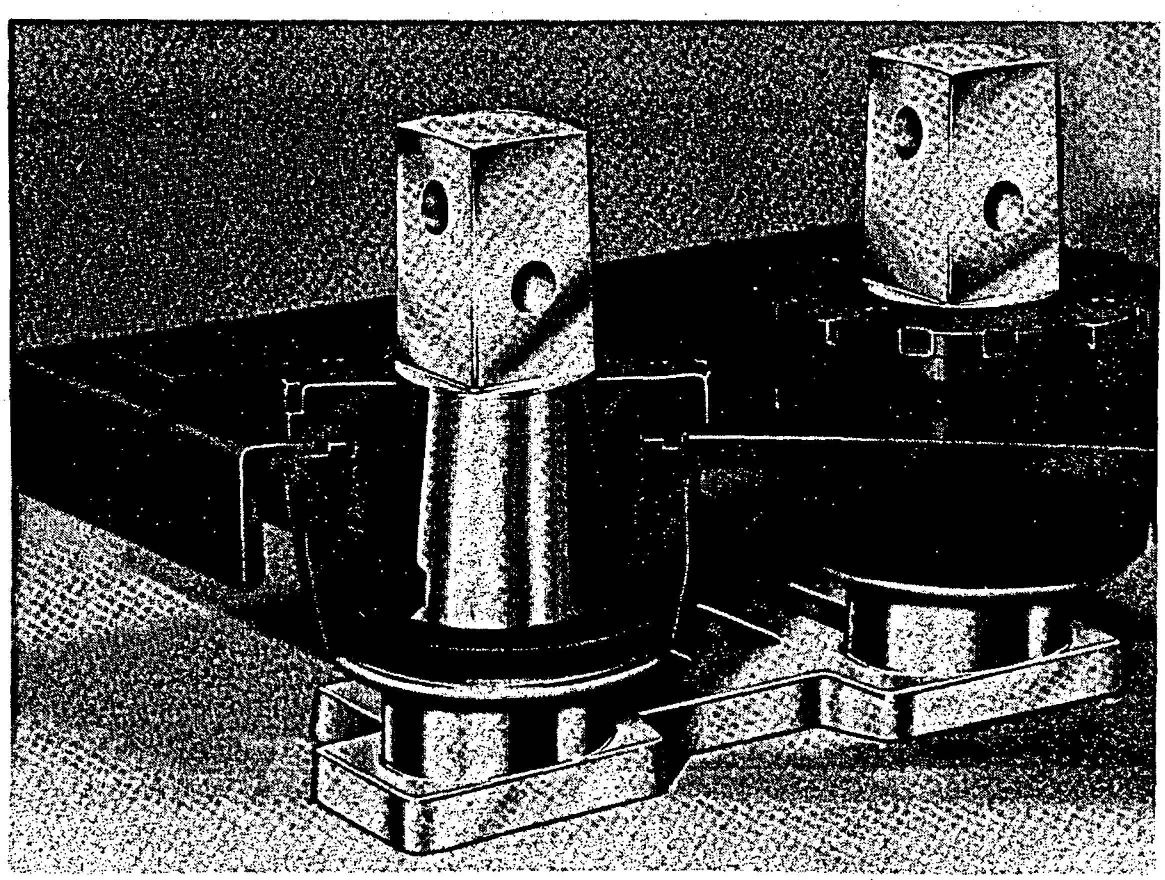

Figure 4. Post, strap, and seal assembly.

them, with opposite polarities for the positive and negative plates. The PbO is converted to PbO_2 in the positive plate and spongy (porous) Pb in the negative plate. The Pb in the negative plate is spongy because expander material is added to accommodate volume changes during the electrochemical reactions.[8]

Separators are installed between the plates to provide a physical separation and yet allow conduction of ions through the electrolyte between electrodes of opposite polarity. A cover completes the containment so that the electrolyte does not escape and contaminates do not get inside. A vent is necessary to provide an opening for electrolyte addition as well as a means for the escape of gases formed during charging. Figures 5 and 6 show a picture and a sketch of a battery with all the essential components[9,10].

Cells are placed in racks designed to support the cells during seismic events and are connected together in banks to form the battery. The batteries are housed in a room designed to provide an environment suitable for the battery.

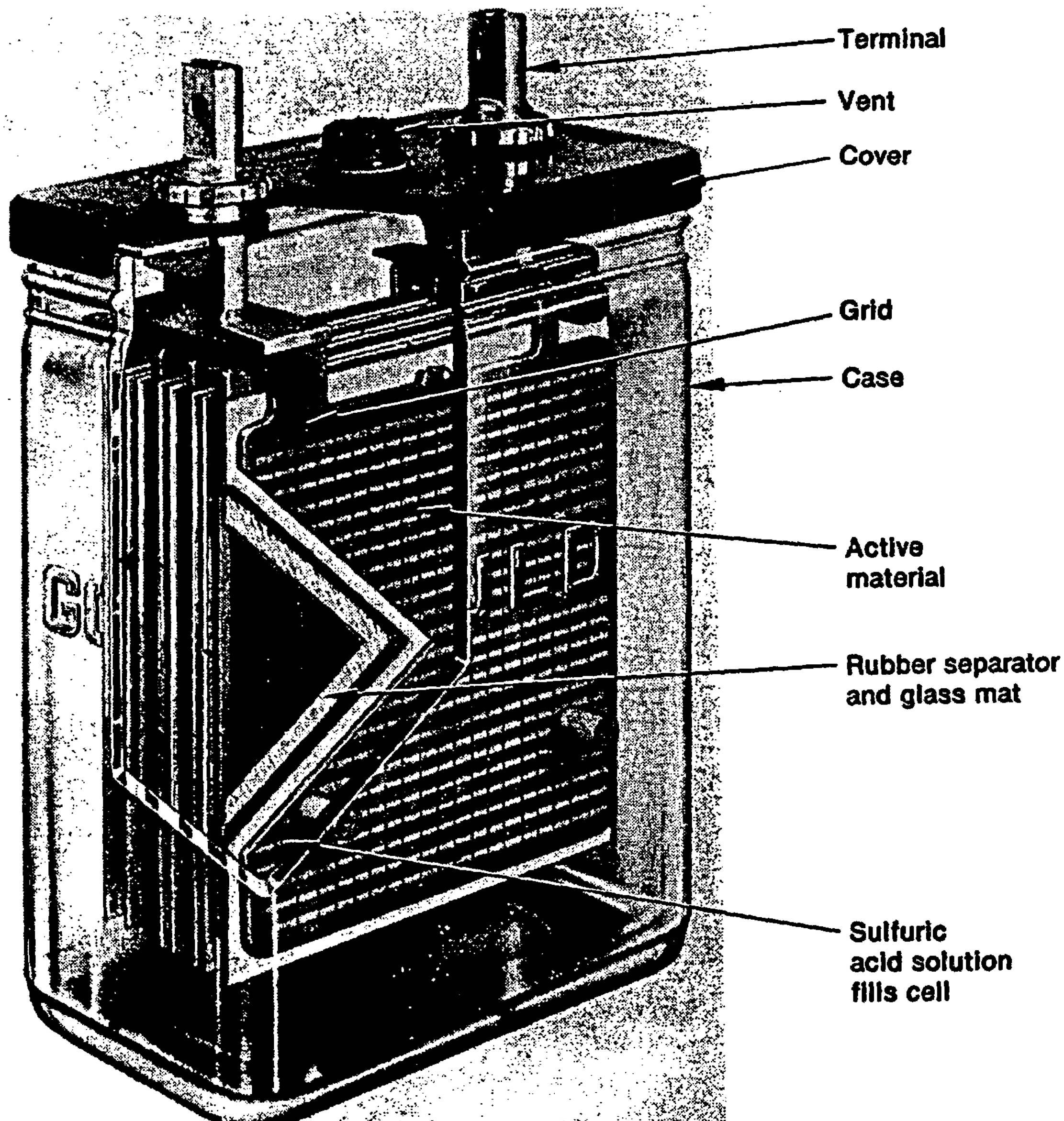

Figure 5. Lead-acid battery (taken from Reference 9).

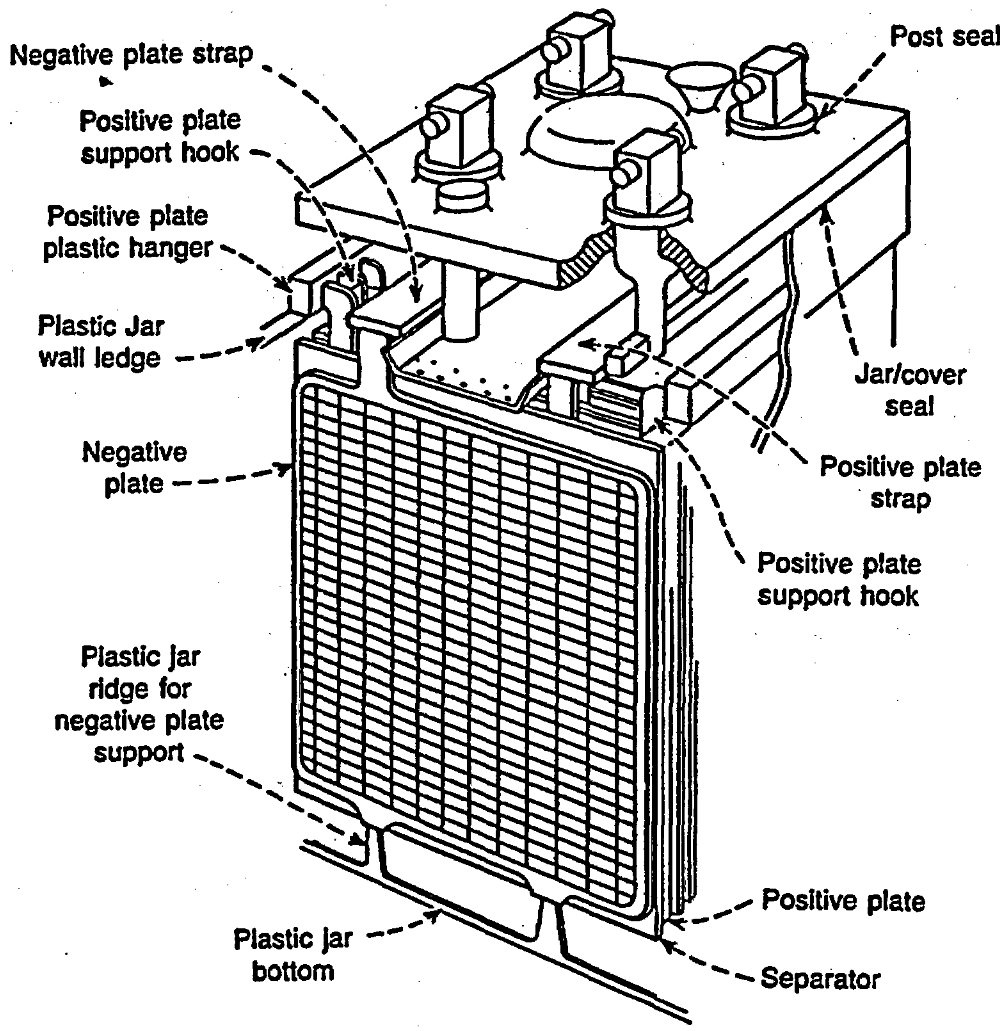

Figure 6. Typical lead-acid battery for telephone reserve use (taken from Reference 10).

3. MATERIALS OF CONSTRUCTION

Major U.S. manufacturers of lead-acid storage batteries used in nuclear power plants were contacted with respect to materials of construction of lead-calcium batteries. The major components of all batteries are made of essentially the same material, with the exception of the terminals, container, and cover. Some terminals are made of only a lead-calcium alloy, while others are made of a lead-calcium alloy with a copper insert. The copper inserts increase conductivity but must be processed correctly to avoid galvanic action, bringing on early failure. Containers are made of Styrene Acrylonitrile, or Polycarbonate and Acrylo Butadiene Styrene. Table 1 lists the major components and the materials of construction.

The components most susceptible to aging are the electrodes (plates) and the lead-calcium conductors at the top of the battery. Aging of these components leads directly to loss of capacity or catastrophic failure.[11,12] Containers may age and fail; however, operating experience has shown that these failures have resulted in slow leaks of the electrolyte and have not resulted in decreased capacity of the cells as long as the electrolyte level and specific gravity are maintained. However, a container that is already cracked could be more vulnerable to a seismic event with the existing crack becoming much larger, resulting in a rapid release of electrolyte. Because the cells are connected in a series configuration, the failure of one cell could result in failure of the whole battery. Slow leakage, if not stopped, has the potential to corrode and weaken the supporting battery racks.

Table 1. Lead-acid storage batteries materials of construction

Cell Components	Materials of Construction
Grids (all)	Lead-calcium alloy
Active material	Lead dioxide (positive plate) Lead with expander added (negative plate)
Separator	Rubber/glass mat or microporous polyethylene sheets
Electrolyte	Sulfuric acid and water with density of 1.200 to 1.220 g/cc
Vent	Fused alumina funnel
Top conductor	Lead-calcium alloy
Terminals	Lead-calcium alloy or Copper inserts in lead-calcium posts
Container and cover	Polycarbonate (LEXAN), Styrene acrylonitrile (SAN) Butadiene styrene (some covers)

4. STRESSES AND AGING MECHANISMS FOR BATTERIES

Even though batteries are operated normally in a mild environment, they can be subjected to stresses that cause aging effects. Generally, these stresses may be grouped into five categories: electrical, mechanical, thermal, environmental, and design basis.

4.1 Electrical Stresses

Electrical stresses in batteries are related primarily to improper operation of the battery charger so that the battery is either undercharged or overcharged. Overcharging results in excessive temperatures and gassing, which are injurious. When energy is put into a battery, as in charging, it is dissipated by three different mechanisms: (a) the electrochemical reaction that charges the active material of the battery, (b) the generation of heat as the result of current passing through the internal resistance of the battery (I^2R), and (c) hydrolysis of the water of the electrolyte (decomposing it to hydrogen and oxygen) due to excess current not utilized in charging the active material (known as gassing). When the battery is in a discharged condition, comparatively high charging rates can be utilized, and little gassing occurs. As the charging progresses, the more accessible portions of the active material become fully charged, the total amount of uncharged active material is reduced, and the charging is confined to the more remote portions where acid diffusion is restricted. The rate the remaining uncharged material can be charged is correspondingly reduced. Any charging current in excess of what can be used will produce a corresponding amount of gas. Usually the positive plates become charged in advance of the negative plates; thus, for batteries with greater negative plate capacity than positive, gassing will, for a time, be more evident at the positive plates. When both sets of plates are fully charged, the volume of hydrogen given off at the negative plates will be twice that of the oxygen given off at the positive plates. When gassing begins toward the end of charge, the rate of heat generation increases considerably beyond that due to the I^2R loss, owing to causes not fully understood. Hence, gassing and heating become greater after the battery is charged.[8] Gassing tends to dislodge the active material from the plates, when bubbles are formed below the surface, and may reduce the capacity of the battery, depending upon the rate of discharge. Capacity loss will be more noticeable at extended, low discharge rates than at short, high discharge rates. Gassing also accelerates corrosion of the positive-plate grids and plate straps because oxygen is formed at the positive plates, thus creating an oxidizing environment.

Excessive temperatures increase "local action", especially at the negative plates, requiring increased overcharge at the positive plates, involving excessive gassing and further heat development. Local action is the discharging (electrochemically) of the active material due either to some impurity in the electrolyte, which reacts with the active material chemically, or to the deposit of some impurity on a plate, which gives rise to a sufficient difference in the electromotive force (emf) developed at different points of the plate to produce local currents between those points through the electrolyte. Local action at the positive plates is due generally to the accidental introduction of an impurity in the electrolyte, such as iron or chlorine, which enters into a direct chemical reaction with the lead dioxide. Local action may be produced at the negative plates by a similar reaction with an impurity in the electrolyte, such as an oxidizing agent. Some chemical reagents introduced into the electrolyte, such as chromium, act as an oxygen carrier and will alternately discharge the positive and negative plates. From a practical point of view, the most important form of local action is that due to the deposit of a metallic impurity on the negative plates, causing the discharge of the active material by local currents. In this state, the specific gravity will be lowered, due to the chemical reactions, and the battery will appear to need charging. However, the positive plates are still fully charged and subsequent charging will result in overcharging the positive plates along with gassing and increased temperatures, as previously discussed. Local action increases with increased temperature and specific gravity of the electrolyte.

Excessive temperature also accelerates corrosion of the lead and causes deterioration of separators and hard-rubber components. Temperature effects will be discussed in more detail in a following section.

Consistent undercharging results in a gradual running down of the cells. When undercharging has been prolonged, lead sulfate is formed at both the positive and negative plates. The lead sulfate occupies more space than the original material, and an excessive amount of it strains the plates. Eventually, buckling of plates may result from the stresses. Consistent undercharging usually results in one or more of the cells becoming exhausted before the others, and some of these may become reversed (electrically) by the other cells of the battery. When this occurs, the most obvious remedy is to charge the battery until all the cells are again in normal condition.[7] This will result in overcharging some of the cells with the detrimental effects that were discussed above.

Ripple (harmonic fluctuations in the voltage) from the battery charger can also stress the battery. Excessive ac ripple causes stresses at the plates with results that are similar to overcharging. Ripple may be a larger problem than had been thought earlier as some studies have shown this to accelerate corrosion at the interface between the grid and active material.[7] The corrosion material occupies more volume than the active materials, producing stresses in the plates.

4.2 Mechanical Stresses

Mechanical stresses usually are related to handling, seismic bracing, or excessive growth of the positive plates. Handling, either during installation or during maintenance, can injure or disable the battery. Mishandling during installation can result in cracked cases and leakage of the electrolyte, which, if undetected, could result in corrosion of the battery racks and a low electrolyte level with decreased battery capacity. Mishandling during maintenance and installation can result in damaged or broken terminals and connectors. Overtorquing, for example, can cause broken terminals and connectors resulting in catastrophic failure of the battery.

Seismic bracing, if not properly designed or installed, can cause stresses to the battery cases resulting in cracks and leaks. In addition, improper seismic bracing (either design or installation caused) can cause the battery to experience larger-than-expected stresses during a seismic event and then possibly fail and not be available to provide needed power after the event.

To ensure that the batteries are always in a full state of charge, they are "floated" at 2.15 to 2.25 V per cell, depending upon the manufacturer and battery model. Under float conditions, lead dioxide is the thermodynamically stable solid phase at the positive plates. Consequently, the lead or lead-alloy grid is oxidized, along with the pellets or active material, to lead dioxide, which has a specific volume 21% greater than lead. Therefore, the corrosion product induces stresses in the lead substrate from which it was formed. The induced stresses cause growth of the grid, which eventually results in failure of the battery. The effect of grid growth is illustrated in Figure 7, which shows a severely corroded lead-calcium plate overlayed with a noncorroded grid to show original dimensions. This grid has grown to such an extent that cracking of the lead-dioxide pellets (active material) and loss of contact with the grid members have occurred. Battery manufacturers usually design the grids such that the orientation of the metal crystals results in plate growth mostly in the vertical direction. Space is left between the bottom of the grid and the battery case to allow for plate growth during the design life of the battery.

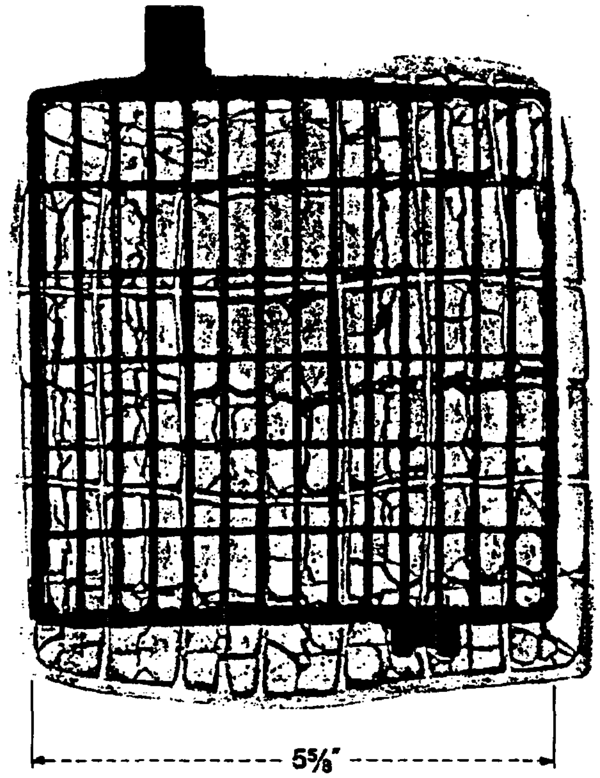

Figure 7. Severely corroded pasted lead-calcium grid with overlayed bare grid to show initial dimensions (taken from Reference 10).

The growth rate is generally accepted by battery manufacturers as being 0.001 to 0.0015 in. per inch per year. However, the growth rate is dependent upon all the factors that affect corrosion, such as temperature, impurities, and specific gravity of the electrolyte. This plate growth can cause loss of contact between the active material and the grid, with decreased battery capacity as the result. In addition, excessive positive plate growth can also result in cracking of the battery cases, and rupture of the covers and terminal seals.

4.3 Thermal Stresses

Thermal stresses, whether caused by internal sources as previously mentioned or by the room temperature, are probably the most detrimental with respect to accelerating aging of batteries. Temperature is a significant factor in the rate of plate growth, corrosion of the lead grids and straps, and deterioration of the the separators.[13] A major battery manufacturer has stated that an increase in ambient temperature from 77 to 95°F reduces the life of a battery by 50%.

The principal corrosion reactions that occur within the cell at rest (neither being charged or discharged) are:

At the negative:

$$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$$

$$Pb + H_2O \rightarrow PbO + 2H^+ + 2e^-$$

At the positive:

$$PbO_2 + 2H^+ + 2e^- \rightarrow PbO + H_2O$$

These reactions are dependent on pH and the amount of sulfate present. However, some of each will occur resulting in oxidation of the battery. These reactions are accelerated by heat.[14]

When a fully charged battery is floated, as batteries are at nuclear plants, some gassing occurs with oxygen being formed at the positive plates and hydrogen being formed at the negative plates. The principal corrosion occurs at the positive plate, because it is in an oxidizing environment and the negative plate is in a reducing environment. This oxidation, at the positive plate, occurs first at the grain boundaries resulting in brittleness and fragility. Positive terminals are also subject to corrosion, embrittlement, and then possible failure. Oxidation and corrosion is enhanced at the electrolyte-air interface at the top of the battery where conditions such as vapors and gases are present that are conducive to corrosion and oxidation. All of these reactions are accelerated by heat. This embrittlement causes the battery to be susceptible to failure due to vibrations and shaking such as would occur during a seismic event.[12] Thermal aging usually is a slow process with a slow loss of performance until near the end of life. Catastrophic failure to deliver energy may then result if the battery is subjected to a seismic event.

4.4 Environmental Stresses

The most likely environmental stresses contributing to degradation of batteries are impurities, dirt, moisture, oxidation, and temperature. Temperature and internal oxidation have already been discussed.

Impurities that reach the electrolyte, whether through the water that is added or from some other source, cause many problems. Shedding of positive active material, corrosion of the positive grid and terminal, and hydrolysis (breaking down of water into hydrogen and oxygen) are some of the more significant problems. Impurities, especially the organic type, accelerate corrosion. The organic matter (sugars, acids, paper, etc.) is oxidized to acetic acid, the acetic acid reacts with the lead, and lead acetate (soluble) is formed. The negative lead-acetate ion migrates to the positive plate and attacks the lead. Quickly, the lead looses its mechanical strength. Severe damage may result with a level of 0.1% organic impurities in the electrolyte. Iron is the most common inorganic impurity. Iron is oxidized at the positive plates and reduced at the negative plates, resulting in total discharge of the battery. The following equations can occur:

At the positive:

$$PbO_2 + 2FeSO_4 + 2H_2SO_4 \rightarrow$$
$$PbSO_4 + Fe_2(SO_4)_3 + 2H_2O$$

At the negative, there are two possible reactions:

$$Pb + Fe_2(SO_4)_3 \rightarrow PbSO_4 + 2FeSO_4$$

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2$$

Effects can be noted at concentrations as low as 0.012%. Other impurities of concern are: Manganese, Chlorine, Barium, Copper, Zinc, Antimony, Tungsten, and Mercury. The solution to these problems is to always use distilled water when adding water to maintain the electrolyte level.

Dirt and moisture on the top of the cell can result in low resistance paths between the positive and negative terminals and discharge the cell. Low resistance paths to ground can also violate grounding criteria. Oxidation/corrosion of terminals can result from moisture and also from gassing caused during battery charging. The corrosion also causes high resistance connections at the terminals and can impair the ability of the battery to deliver the required energy.

Correct maintenance resolves most environmental-stress problems and alleviates others related to electrolyte level and state of charge of the battery. Maintenance also allows a history of the battery to be created, for determining the state of the battery.

4.5 Design Basis Event Stresses

The seismic event is the only applicable design basis event that affects batteries. Batteries are located in a mild environment in the battery room where spray or steam environments are not expected. They may be subjected to moderate temperature and humidity conditions during design basis events, but these conditions would not vary much from normal conditions nor would they last for long periods.

The battery's capability to withstand a seismic event does appear to change with aging.[12] Embrittlement of the lead at the positive terminal appears to develop as the battery ages, thus increasing its susceptibility to the seismic event. Broken posts and bus bars could also occur during a seismic event.[12] These events would result in catastrophic failure where the battery would have no output. However, batteries qualified to IEEE Std-535 and properly maintained should not be vulnerable to seismic events less severe than the level to which they were qualified. Cracking of the cases may occur with a slow leakage of electrolyte. However, this would not result in an immediate loss of capacity unless the cracks grew to be very large or portions of the case broke off allowing the electrolyte to quickly escape. Corrosion of the battery racks could result from slow leakage that was allowed to continue for a long period of time and result in the racks not being able to withstand a severe seismic event.

Table 2 provides a tabulation of the stresses discussed above, type of aging that results, and ultimate effect of the stress on battery operation. Table 3 summarizes the effects of the stresses upon the materials of construction listed in Table 1.

4.6 Summary of Stresses

The single most predominant stress mechanism related to aging in batteries appears to be thermally induced oxidation of the grids and top conductors. Oxidation of the grids causes them to grow or swell. This, in turn, results in poor contact between the grid and the active material resulting in decreased capacity of the battery. Grid (plate) growth ultimately results in stressing the container and covers; causing cracks to develop in the container, and loss of the electrolyte. Oxidation of the top conductors (lead) causes them to become brittle and susceptible to breaking during seismic events.

Table 2. Tabulation of stresses and effects

Stress	Effect of Stress on Component	Effect on Operation
Electrical Stresses		
Overcharging	• Excessive temperature • Accelerates corrosion	• See thermal stresses
Undercharging	• Buckling of plates	• Reduced capacity or Battery failure
AC ripple	• Excessive temperature • Accelerates corrosion	• See thermal stresses • Reduced capacity
Mechanical Stresses		
Handling	• Cracked cases • Broken connectors/terminals	• Leaking of electrolyte • Battery failure
Seismic bracing	• Cracked cases	• Leaking of electrolyte
Positive plate growth	• Cracked cases • Poor contact between lead grid and active material	• Leaking of electrolyte • Reduced capacity
Thermal Stresses		
Overcharging	• Acceleration of corrosion of positive grids, and straps, and terminals	• Reduced capacity
AC ripple (internal heating)	• Acceleration of plate growth • Deterioration of separators • Embrittlement of positive terminals	• See plate growth • Battery failure • Battery failure
Elevated ambient temperature	• Same as above	• Same as above

Table 2. (Continued)

Stress	Effect of Stress on Component	Effect on Operation
Environmental Stresses		
Impurities in the electrolyte	• Shedding of active material • Corrosion of positive grid • Hydrolysis	• Reduced capacity • Reduced capacity • Reduced capacity
Dirt and moisture on cases	• Low resistance between terminals • Low resistance to ground • Oxidation/corrosion of terminals	• Discharge of cell • Ground faults/shorts • Battery failure • Reduced capacity
Gases	• Oxidation/corrosion of terminals	• Reduced capacity
Seismic event	• Broken positive plates, straps, and/or terminals • Cracked cases • Broken posts/connectors	• Battery failure • Leaking of electrolyte • Battery failure

Table 3. Effects of stresses upon materials of construction

Component	Material	Applicable Stress	Effect of Stress
Grids	Lead-calcium alloy	Thermal	Increased temperatature accelerates oxidation of the lead, which results in plate growth. This causes loss of contact with the active material and stress on the container.
Active material	Lead dioxide and Lead sulfate	Gassing	Dislodges active materal from the plates and loss of capacity.
Separators	Rubber/glass matt	Thermal	Accelerates deterioration resulting in internal short circuits.
Electrolyte	Sulfuric acid and water	Contamination	Chemical reactions cause hydrolysis of the water, which cause loss of electrolyte and sulfuric acid.
Vent	Fused alumina	Mechanical	Breaking of the vent, which would allow contaminates to enter the cell. Also, gas releases would be uncontrolled.
Top conductors	Lead-calcium alloy	Thermal, low electrolyte level	Temperature accelerates corrosion of the lead, which results in embrittlement and susceptibility to breaking. This is enhanced if the electrolyte level is low and exposes the lead.
Terminals	Lead-calcium alloy, copper inserts in lead-calcium alloy	Oxidation, corrosion	Corrosion results in poor electrical contact with the external busses.
Container and cover	Polycarbonate, Styrene acrylonitrile, or Polycarbonate and Acrylo Butadiene Styrene	Mechanical, Plate growth	Cracking of the container resulting in loss of electrolyte.

5. OPERATING EXPERIENCE AND TEST RESULTS

The battery experiences summarized in the NRC Information Notices, as well as results of battery tests, are discussed below. The failures are identified and discussed in some detail.

The NRC Information Notice No. 83-11 relates two instances of cracked and leaking cases (containers) with Gould FTA-15 batteries at the Haddam Neck plant. Two cells were discovered to be leaking on September 19, 1982. Further examination showed casing cracks that did not extend through the wall on 11 other cells. The licensee declared the battery bank inoperable and completely replaced it. The cells were about 15 years old and are a design that has not been manufactured for about 10 years. The Information Notice pointed out that other examples of cells failing because of swollen plates and cracked cases have been identified. The Information Notice then referenced six LERs involving instances of battery case cracking, five apparently bearing some similarity to the Haddam Neck failure. The Information Notice stated that, "A pattern is developing of spontaneous failure of old batteries that suggests a seismic event could cause a common-mode failure of the plant DC system." The Information Notice concluded by stating:

> "Although no seismically induced battery failure has occurred to date, the serious consequences of such a failure are worthy of concern. Several postulated examples follow: A seismic event might accelerate cracking of the case resulting in loss of electrolyte and complete loss of battery. A seismic event might cause accelerated cracking of embrittled plates or loss of lead-dioxide coating of plates resulting in substantial drop in battery capacity almost immediately. A complete loss of the DC system would put the plant in a unanalyzed condition."[15]

The NRC Information Notice No. 84-83 discusses solvent-induced case cracking at the Byron and Braidwood plants in April 1984. The batteries were NCX-1200 type with styrene-acrylonitrile (SAN) cases manufactured by GNB (previously Gould) Batteries, Inc. The crescent-shaped cracks were attributed to the use of a solvent, trichlorethylene, to remove anticorrosion grease and clean the battery posts during rework of the intercell connections.[16] Further, 4 cells were discovered leaking and 39 cells had non-through-wall cracks at the Fitzpatrick plant in March 1983. These cells were also manufactured by GNB Batteries, Inc., with cases constructed of SAN. GNB Batteries, Inc., suggested that the cracking was caused by the application of hydrocarbon-based grease to the vinyl straps on the battery rack, presumably to permit the cells to slide over the racks more easily and facilitate installation of the cells. The hydrocarbon oil in the grease acted like a solvent and attacked the cell cases constructed of SAN. "Tests have shown that some commonly used solvents will induce almost instantaneous cracking of battery cases."[16] It is interesting to note that GNB now uses only SAN because of problems experienced in sealing polycarbonate containers with the cover.

Flaking of the internal lead along with sediment in the bottom of the cells was reported in NRC Information Notice No. 86-37.[17] Batteries at the Rancho Seco Nuclear Power Plant exhibited flaking of the cell plates and the hook area of the plates where they are supported. An inspection 1 year earlier by the battery vendor (not identified) did not reveal abnormal degradation. The batteries have subsequently been replaced. This problem is similar to the oxidation discussed previously, where the lead either swells as a result of the oxidation and results in plate growth or becomes embrittled and then is subject to breaking during a seismic event. A conclusion of the Information Notice was that seismic-fragility test results of some naturally aged batteries[12] combined with the observed flaking suggest the importance of examining the internal connections between the plates, strap, and post.

Degraded cells were observed at the Duane Arnold plant in September 1986.[18] A white substance was observed in the electrolyte of some of the cells of the 250 V battery. The vendor (unidentified) was asked for assistance and found three plates separated in one cell and 50% erosion of the plate-to-bus-bar connection in eleven other cells. Subsequently, the licensee discovered two other cells with degradation. The cells were about 15 years old (installed in 1971) and are no longer manufactured. The vendor examined the failures and concluded that the problem was caused by accelerated aging due to temperature and not by a manufacturing defect. The problem was further confined to plates of the Planté design (active material is electrochemically formed on the plates). This problem is similar to the degradation observed by Sandia National Laboratories in seismic-fragility tests of naturally aged batteries (discussed later in this section).[12]

Improper float voltages were reported in NRC Information Notices Nos. 86-37 and 85-74.[17,19] Float voltage was either too low resulting in undercharged batteries or too high with the potential to overcharge the batteries. Undercharged batteries contain less capacity than assumed and may not be able to deliver the required energy when demanded. Overcharging can be detrimental to the life of the battery, as previously discussed. Both of these problems can be corrected easily by readjusting the float voltage. Both NRC Information Notices 86-37 and 85-74 emphasized the need for readjusting the float voltage when battery cells are changed or when degraded cells are jumpered. In addition, it was stated, "Although batteries contain no moving parts, considerable care and attention to detail is required."[19] The NRC Information Notice 85-74 also reported other battery-related problems. Procedural problems were reported, such as:

- Performing the rated-load discharge test at a discharge rate significantly less than the manufacturer's recommended rated-load discharge rate for the 8-h period of the test
- Failing to correct specific gravity measurements for electrolyte temperature and level
- Not comparing intercell resistance values with previous values
- Not conducting equalizing charges.

In addition, battery records were not properly maintained.

Naturally aged 12-y old NCX-2250, 10-y old LCU-13, and 10-y old FHC-19 lead-calcium cells; and naturally aged 13-y old FKR-25 and 23-y old EMP-13 lead-antimony cells were inspected and dynamically tested by Sandia National Laboratories (SNL) as part of a NRC-sponsored program.[4,12,20,21,22] The purpose of the tests was to determine seismic failure modes and thresholds of naturally aged cells and to identify the dominant aging mechanisms. The test program consisted of an initial inspection of the cells, pre-seismic discharge tests at the 3-h rate (as stated by the manufacturer), a seismic test program for those cells that passed the pre-seismic inspection and tests, and post-seismic inspections and discharge tests at the 3-h rate.

The seismic test program consisted of shake tests while the batteries were under load at the 1-h rate. Two different acceleration patterns were utilized. The NCX-2250, FKR-25, and EMP-13 cells were subjected to a graduated series of increasing zero-period accelerations (ZPA) until either the shake-table limits were reached (about 2 g) or until electrical failure of the cells occurred. The FHC-19 and LCU-13 cells were subjected to a two-stage approach. The first stage exposed the cells to a simulated seismic event with peak ZPA up to approximately 1.5 g. The second stage exposed two cells that passed the first stage to a higher seismic intensity with a ZPA of approximately 2 g. Table 4 shows a summary of the tests and inspections. Test results showed that 67% of the NCX-2250 cells failed to maintain either 80% of rated capacity or cell potential of 1.75 V during a series of seismic events, while 67% of the FHC-19 and 100% of the EMP-13 cell failed the post-seismic discharge test. All of the FKR-25 cells passed the seismic tests and 75% passed the post-seismic discharge tests. Two FHC-19 and two LCU-13 cells were subjected to a second stage of seismic tests. Of these, one FHC-19 cell failed to hold a 1.75 V cell potential under load immediately before and during seismic testing, while the other cells survived seismic testing but failed the subsequent, 3-h rate, post-seismic discharge test (results are not shown on Table 4). Most of the failures appear to have occurred at imposed g-level loads in excess of a 1-g ZPA. These loads are greater than those required for qualification at most nuclear plants.

Post-seismic examinations showed variable types of degradation, depending upon the cell type. Three of the five cell types (FKR-25, FHC-19, and EMP-13) showed evidence of significant aging of the positive plate material. While plate growth was not large, effects included hard active material that became disconnected from the grids during seismic testing, and corrosion and flaking of the grids. Significant amounts of brittle and corroded positive bus material was present in three of the cell types and could be made to fracture under the stress of moderate hammer blows to the attached posts. For the majority of the NCX cells, the stresses of seismic testing alone resulted in visible fractures of extremely brittle material. Corrosion penetration into buses was observed for all cell types, but varied from about 10% to almost 100% of the cross-section area of the bus, depending on cell type. Except for EMP-13 cells, all negative plates of other cells were in operating condition and seemed to have suffered only minor damage due to aging as they deformed to accommodate positive plate growth. Tables 5 and 6 show summaries of post-seismic examinations of the positive plates and the positive bus, hangars, and posts. The study has concluded that, "In these tests, loss of capacity during or after seismic testing has been due to fracture of brittle and corroded positive bus material, significant loss of positive plate active material, or, in one case, grid fracture and loss of material from the negative plates.

The significant aging effects, in terms of seismic survivability, appear to be:

- Formation of brittle, corroded positive bus material
- Excessive sulfation of positive plate active material.

The formation of brittle bus material appears to be the more significant aging effect as it can lead to abrupt

Table 4. Number of cells tested per program step seismic fragility testing program[a]

Program Step	Cell Type				
	FKR-25	NCX-2250	LCU-13	FHC-19	EMP-13
1. Cells delivered to OHRD	12	20	12	10	20
2. Cells passed visual inspection	12	11	12	10	16
3. Cells conditioned, then discharged at 3-h rate	11	11	12	10	12
4. Cells passed[b] at 3-h rate (pre-seismic)	11	10	12	9	9
5. Cells seismically tested	8	9	7	7[c]	9
6. Cells passed[d] seismic tests	8	3[e]	7	7	9
7. Cells discharged at 3-h rate	8	2[e]	7	6[c]	5
8. Cells passed[b] at 3-h rate (post-seismic)	6	2	7	2	0
9. Cells dissected (P) = passed Step 8 (F) = failed Steps 4, 8, or 6	1(P) 1(F)	2(P) 7(F)	4(P)	1(P) 3(F)	2(F)

a. Adapted from Reference 4.

b. Pass = ⩾80% of rated capacity.

c. One cell was tested twice, as a single cell and in a rack of three cells; hence the apparent discrepancy in the cell count.

d. Pass = Cell Potential ⩾1.75 V.

e. One cell was shipped to Westinghouse R&D center for evaluation (see DAND86-7080, NUREG/CR-4533).

Table 5. Positive plate condition summary seismic fragility testing program[a]

Characteristic		FKR-25	NCX-2250	LCU-13	FHC-19	EMP-13
		Cell Type				
Detrimental	1. Brittle	No	No	No	Yes	No[b]
Active	2. Hard	Yes	No	No	Yes	No[b]
material	3. Pitted	No	No	Yes	No	No
conditions	4. Broken	No	No	No	Yes	No
	5. Obstructed	Yes	No	Yes	Yes	Yes
	6. Disconnected	No	No	Yes[c]	Yes[d]	No
Detrimental	1. Warped	Yes	No	No	Yes	No
grid	2. Corroded	Yes	No	No	Yes	Yes
conditions	3. Flaking	Yes	No	No	Yes	Yes
Active material shore hardness[e]		60	50	45	60	—
Plate growth	1. Thickness (mm)	2.5	0.0	(0.2)	0.0	0.8
or (Shrinkage)	2. Width (cm)	0.1	0.0	0.0	0.7	0.2
per plate	3. Height (cm)	0.1	0.0	(0.1)	0.7	0.1

a. Adapted from Reference 4.

b. A non-brittle material is embedded in a hard, lead button.

c. Thin sheets.

d. Chunks.

e. Type A-2 Hardness meter as used for ASTM D2240-81.

Table 6. Positive bus, hangers and posts-condition summary seismic fragility testing program[a]

Characteristic		FKR-25	NCX-2250	LCU-13	FHC-19	EMP-13
		Cell Type				
Detrimental conditions	1. Fractured[b]	No	Yes	No	No	No
	3. Brittle[b]	No	Yes	No	Yes	Yes
	4. Corroded[b,c]	No	Yes	No	Yes	Yes
	5. Flaking[c]	Yes	No	No	No	Yes
Corrosion penetration through bus cross section (% of conduction area discoloured)		30-40	50-100	<10	40-55	41-55
Relative quantity of large-grain Material		Little	Excessive	Little	Moderate	Moderate

a. Adapted from Reference 4.

b. Bus Material

c. Bus and hanger material

failure of a cell during a seismic event. Excessive sulfation leading to plate hardening and expansion, for the most part, affects the post-seismic discharge capacity and the ability of the cells to be recharged and maintain charge.''[4]

Conclusions reached in the test program support the observations and conclusions in the NRC Information Notices previously discussed.

The present method used to accelerate aging of cells is to expose them to an elevated temperature for an extended period of time. The temperature to be used and the length of the aging period is determined by applying acceleration factors that are given in IEEE Std 535-1986.[23] The supposed predominate aging failure mode is based on positive grid growth and then plate failure. As a part of their investigations, SNL performed an evaluation of accelerated aging of various items of equipment, including batteries and reported the results in NUREG/CR-4301.[24] This report pointed out that another battery failure mode, in addition to plate growth, was found to be evident in naturally aged batteries. This mode, as previously discussed, involves corrosion, oxidation, and embrittlement of the bus bar in addition to plate growth. In fact, plate growth of the naturally aged batteries that were tested was found to be small. Based on these results, the report suggested that a full evaluation and test program was warranted to determine acceptable accelerated aging methods.

Sandia National Laboratories continued their investigation of accelerated aging of batteries by obtaining new Class 1E cells from the three major battery manufacturers of batteries in nuclear plants and testing both pre-aged and accelerated-aged cells. This work is reported in NUREG/CR-4098.[25] Some of the results reported are that formation of brittle positive bus and grid material occurs in artificially aged cells and embrittlement and/or cracking of positive buses and grids was aided by corrosion along large grain boundaries in all cell types tested. The report also concluded that the accelerated aging method given in IEEE Std 535-1979 provides an acceptable procedure for reproducing seismically significant, age-related effects in lead-acid emergency power battery cells, and that grid embrittlement during accelerated aging added the equivalent of five years to the conditional age of the test cells as given by the aging factors in IEEE 535.

In conclusion, the currently used acceleration method of exposing batteries to elevated temperature and applying an acceleration factor as described in IEEE Std 535-1986 provides an acceptable procedure for reproducing seismically significant, age-related effects in lead-acid batteries. These effects are adequately reproduced even though plate growth in naturally aged batteries may not be as much as it is in accelerated-aged battery cells.

The Bell Telephone system uses batteries extensively in a mode similar to nuclear power plants. Bell Telephone maintains batteries in a fully charged state with a float current to be able to provide large amounts of current if all other sources of power are lost, similar to the application in a nuclear power plant. In addition, long life and minimum maintenance are also required of the batteries. They have found the life of lead-calcium batteries to average about 15 years and to be limited by the growth, with time on float, of the lead-calcium alloy positive grids. Grid growth results in cracking of the active material, loss of contact between the active material and the grid, and cracking of the cases.[10,12,26] These conclusions (reported in 1970) support the experience and test results obtained in the nuclear industry.

6. EVALUATION OF BATTERY FAILURE DATA BASES

Data from the LER system, NPRDS, IPRDS, and the NPE data base were analyzed to identify dominant failure causes and their relationship to aging. Each of these data systems have limitations. Only certain failures of safety-related equipment are reported in the LER system because the reporting requirements are determined by each plant's Technical Specifications. The NPRDS reports most safety-related failures, but complete information is available for only a short time period. The IPRDS data are available for only five plants. The NPE is a large system-oriented data base with reports for over 85 plants and covers the time since 1960. However, care must be used in selecting the search criteria if all pertinent data is to be obtained. Data-base events utilized for this report were not restricted to Class 1E batteries or to batteries with lead-calcium plates. Because many of the batteries that have been the subject of an event are of the older types, it is reasonable to assume that a significant percentage were not qualified to current IEEE-535 requirements and some may have been of a lead-antimony design. However, the data-base information is useful in identifying dominate failure causes for batteries and particularly for older batteries that are still installed in nuclear plants.

6.1 Evaluation of LER Data

The LER data included entries beginning January 1976 and ending August 1986. Because batteries at many plants have been replaced since the date of first commercial operation, it was not possible to ascertain the age of the batteries at the date of the LER. Table 7 lists the total number and relative fraction of each type of failure listed in the LERs for all batteries. Low specific gravity of the electrolyte accounted for the largest number of events followed closely by personnel errors, which includes operation, maintenance, and testing. Insufficient charge, defective/weak cells, low electrolyte-solution level, and faulty connectors represented most of the remainder of the events. In several events, natural end of life was a factor, although it is not listed as the primary failure cause. This is particularly true of failure causes such as insufficient charge and defective/weak cells. In addition, defective/weak cells included many reports of cracked and leaking battery containers (cases). Personnel errors were also a factor in other failure causes. Low specific gravity, for example, was often caused by not following established maintenance procedures properly.

Table 7. Battery failure events reported in LERSs

Failure Cause	Number	Percentage
Low specific gravity	67	27
Personnel (operation, maintenance, testing)	52	21
Insufficient charge[a]	27	11
Defective/weak cells[a]	22	9
Low electrolyte solution level[a]	14	6
Faulty connections[a]	13	5
Defective procedures	11	4
Charger malfunction	9	4
Design, fabrication, construction	8	3
High electrolyte solution level	8	3
Unknown causes[a]	5	2
Corrosion[a]	4	2
Short circuit[a]	4	2
Normal wear/natural end of life[a]	3	1
Extreme environment	1	<1
	248	100

a. Aging effects may have contributed to the failure cause.

6.2 Evaluation of NPRDS Data

The NPRDS data from 1973 through 1985 were utilized for this evaluation. Table 8 lists the total number and relative fraction of failures for each failure cause. Wearout is the most common failure cause with the other failure causes being about equal. The number of events with an unknown failure cause was high, nearly the same as the number of wearout failures. The

Table 8. Battery failure events reported in NPRDS

Failure Cause	Number	Percentage
Wearout[a]	28	36
Unknown[a]	24	31
Manufacturing defect	6	8
Engineering/design	5	6
Incorrect procedure	5	6
Installation error	4	5
Maintenance/testing	4	5
Other devices	2	3
	78	100

a. Aging effects may have contributed to the failure cause.

NPRDS does not have specific categories for failures such as low specific gravity, high or low electrolyte level, and defective or weak cells. Consequently, both the wearout and unknown causes in the NPRDS are probably higher than the corresponding LER failure causes.

Figure 8 shows the number of battery failures reported in NPRDS as a function of years to failure. There are a significant number of failures in the first year followed by a period of fewer failures, then a trend toward high failure rates beginning in about the fifth year and lasting until the eleventh year. This is consistent with the "burn-in"-type problems at the beginning of operation, a period of relatively trouble-free operation, and then an increase in failures due to age and use of the batteries.

Figure 9 shows the number of failures labeled "wearout" as a function of years to failure. The pattern of these failures is nearly identical to the pattern of the total failures. The indication is that age-related failures begin after about 5 to 6 years. Failed batteries were then replaced over a period of several years with a subsequent decrease in failure rate to a low value at about 11 years.

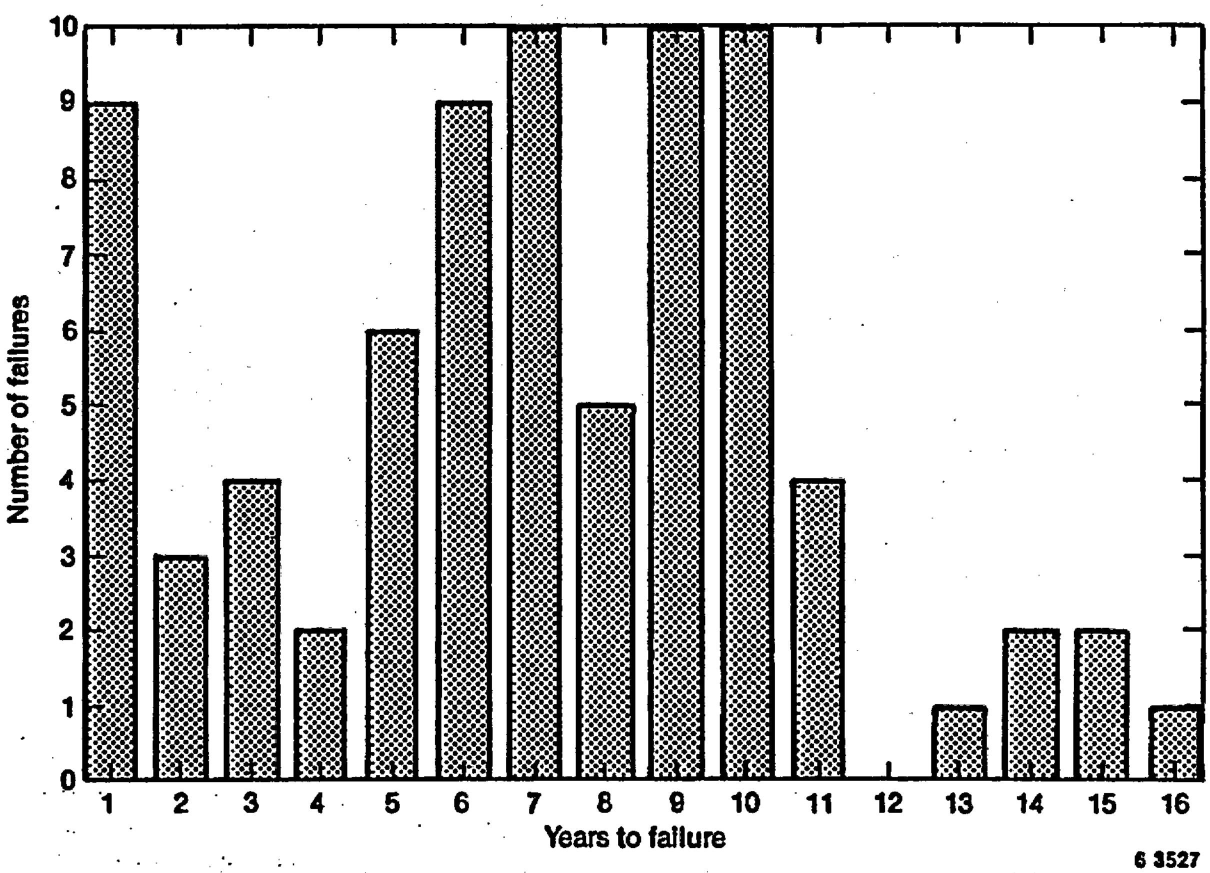

Figure 8. NPRDS reported battery failures (all failures).

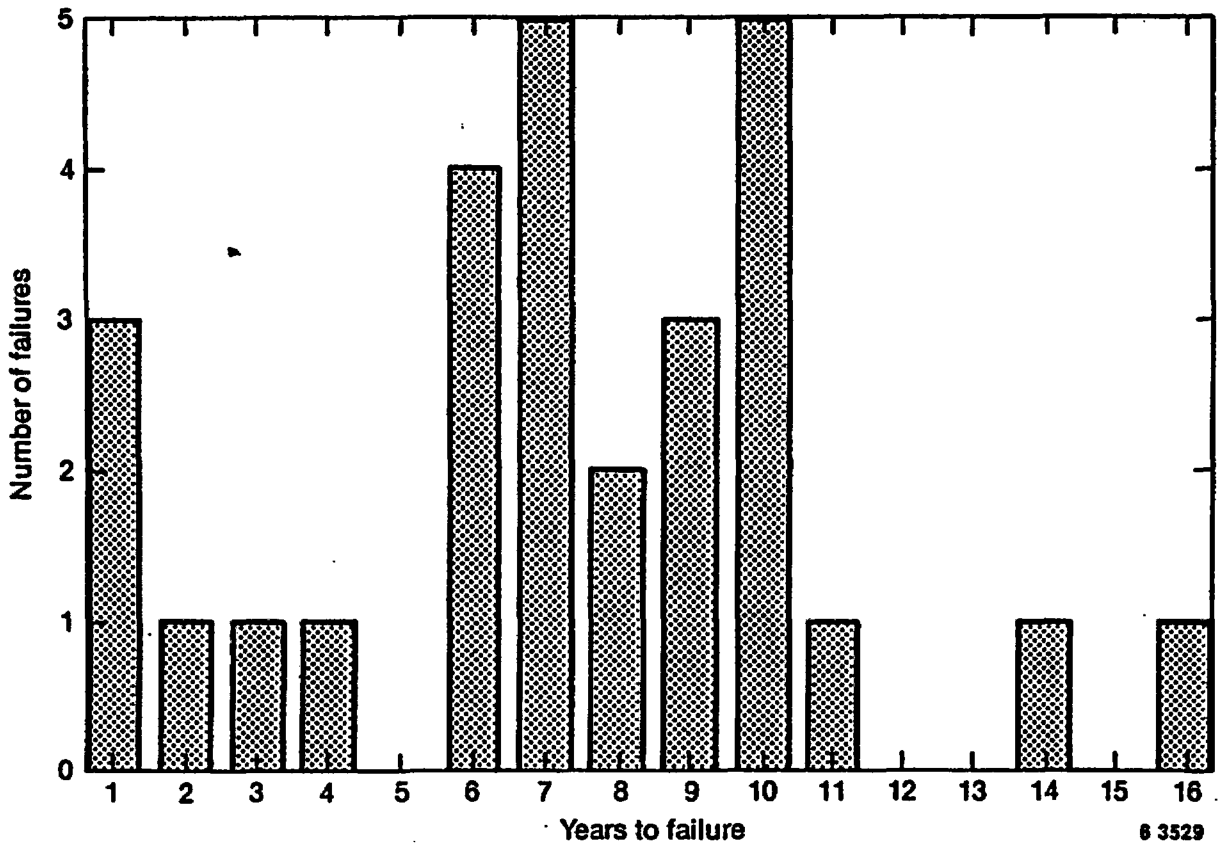

Figure 9. NPRDS reported battery failures (wearout failures).

6.3 Evaluation of IPRDS Data

An evaluation of the IPRDS data has been published by the Oak Ridge National Laboratory (ORNL) (Interim Report, NUREG/CR-3831).[27] This inplant data comes from only five plants. Events were listed in categories and classified as being either catastrophic, degraded, or incipient. Table 9 lists the total number and relative fraction of failures for each failure cause. It was surprising to find that the most common failure was a ground because the other data bases did not identify this as a major cause of failures. Other significant failures were faulty indication, corrosion/dirty/dust contamination, and low cell voltage detected. Because data for personnel, procedural, and end-of-life causes were not provided in the ORNL report, they do not appear in Table 9. Some of the differences between these results and the LER and the NPRDS results discussed above may be due to the limited population of plants covered by the IPRDS study.

6.4 Evaluation of NPE Data

The NPE data for both BWR and PWR plants from the period of 1960 through 1985 was used in the evaluation. Failure causes were established and events were then categorized, as shown in Table 10. "Operator error/defective procedures" and "Low performance/faulty batteries" were the dominant failure causes. "Cracked cases/leakage" and "Poor connections" were also significant failures. Because "Low performance/faulty batteries" includes events such as low specific gravity and low voltage, these failure modes are consistent with the type of failures observed in the review of LERs and with that expected for batteries.

6.5 Conclusions Relating to Data Base Analysis

A review of Tables 7, 8, 9, and 10 shows that events which could be classified as degraded and incipient failure conditions account for most of the events. These events include low specific gravity, insufficient charge, cracked cases/leakage, corrosion, defective/weak cell, and faulty connections. Table 7 shows that low specific gravity is the largest of these events, accounting for about a quarter of all reported events. However, this

Table 9. Battery failure events reported in IPRDS

Failure Cause	Number	Percentage
Catastrophic		
No output	1	1
Inadequate output	7	7
Degraded		
Will not hold charge	8	8
Low cell voltage detected	11	10
Ground detected	33	31
Incipient		
Improper environment (temperature, humidity, etc.)	3	3
Leakage	6	6
Corrosion	15	14
Faulty indication	22	21
	106	101

Table 10. Battery failure events reported in NPE

Failure Cause	Number	Percentage
Unknown/other[a]	36	21
Operator error/defective procedures	33	20
Low performance/faulty batteries[a]	33	20
Battery charger malfunction	17	10
Cracked cases/leakage[a]	12	7
Poor connections[a]	10	6
Maintenance and construction	9	5
Ground/shorts[a]	8	5
Braces and supports	6	4
End of life[a]	5	3
	169	101

a. Aging effects may have contributed to the failure cause.

should be expected because specific gravity is an indicator of the batteries state of charge, is relatively easy to measure, and is measured at regular intervals. Because it is one of the most frequently measured parameters, it is also reported most often. Personnel error is another common event, representing 21% of the events in Table 7. To what extent personnel errors in performing operations, maintenance or testing of the batteries lead to the occurrence of other errors is not known, but the possibility exists for this to be a significant factor also.

After their initial operation, total battery failures and wearout failures appear to peak between 6 and 11 years operation, as shown in Figures 8 and 9. These age-related failures are probably caused by events such as plate growth, grid and strap embrittlement, deterioration of separators, and cracking of cases. Some newer batteries that are qualified to IEEE Std 535-1986,[23] which requires batteries to pass seismic tests after being aged to the end of qualified life, have a qualified life of 10 years (some manufacturers have qualified batteries for 15 years or greater), at which time these batteries would have to be replaced or qualified life would have to be extended. Because these replacements would not be classified as a failure and more reliable operation should result from the more stringent qualification, the 6-to-11 years peak in failures could decrease in magnitude or be extended in time as the newer batteries are installed.

7. BATTERY MAINTENANCE, TESTING, AND MONITORING

The NRC guidance for battery maintenance is provided in Regulatory Guide 1.129, "Maintenance, Testing, and Replacement of Large Lead Storage Batteries for Nuclear Power Plants."[28] Regulatory Guide 1.129 endorses IEEE Std 450-1975 with certain exceptions, one of which requires a "service test" to be performed during refueling operations or at some other outage, with intervals between tests not to exceed 18 months. The IEEE Std 450 has subsequently been revised and the latest issue is IEEE Std 450-1980, "IEEE Recommended Practice for Maintenance, Testing, and Replacement of Large Lead Storage Batteries for Generating Stations and Substations."[29] This standard specifies monthly (at least), quarterly, and yearly inspections as well as several capacity tests. Inspections include visual inspection for cracks, leaks, cleanliness, and corrosion; checking tightness of bolted connections and integrity of the battery racks; and measuring electrolyte levels, ambient and electrolyte temperatures, specific gravity, battery and cell voltages, and charger output. Capacity tests are used to (a) determine whether the battery meets its specification or the manufacturer's rating, or both; (b) periodically determine whether the rating of the battery, as found, is holding up; and (c) if required, determine whether the battery meets the design requirements of the system to which it is connected. Capacity tests include acceptance tests to verify the batteries ability to meet the manufacturers rating or the purchase specification's requirements, performance tests to determine capacity, and service tests to verify that the battery satisfies the design requirements of the system. Inspections and capacity tests are summarized in Tables 11 and 12. Further, it is recommended that a battery be replaced when its capacity has decreased to below 80% of the manufacturers rating, where capacity is the ratio of the actual time to rated time to reach a specified terminal voltage during a discharge test. "A capacity of 80 percent shows that the battery rate

Table 11. Inspection recommended by IEEE STD 450-1980

Inspection	Frequency
Visual	
General appearance and cleanliness of battery and battery area	M,Q,Y
Cracks in cells or leakage of electrolyte	M,Q,Y
Individual cell condition	Y
Corrosion of terminals or connectors	M,Q,Y
Tightness of bolted connections	Y
Integrity of the battery rack	Y
Condition of ventilation equipment	M,Q,Y
Measurements	
Charger output	M,Q,Y
Electrolyte levels	M,Q,Y
Ambient temperature	M,Q,Y
Pilot cell: voltage, specific gravity, and electrolyte temperature	M,Q,Y
Each cell: voltage, specific gravity	Q,Y
Representative cells: electrolyte temperature	Q,Y
Total battery terminal voltage	Q,Y

M - At least Monthly

Q - Quarterly

Y - Yearly

Table 12. Capacity tests recommended by IEE STD 450-1980

Capacity Test	Frequency
Acceptance test	At the factory or upon initial installation
Performance test	Within first 2 years of service; 5 years intervals thereafter; Annually after signs of degradation
Service test	As required by the User (Regulatory Guide 1.129 recommends this test at refueling or other outages, but not to exceed 18 months.)

of deterioration is increasing even if there is ample capacity to meet the load requirements."[29]

The parameters/indicators in Tables 11 and 12 that are monitored (visually or measured) are functional indicators of battery degradation. The primary indicator of battery degradation is the capacity tests of Table 12, which indicates the ability of the battery to provide rated output. Because capacity tests are performed infrequently, the measurements in Table 11, such as specific gravity, voltages, and electrolyte level provide a more current indication of battery condition. Visual inspections for general condition, cracks, corrosion, and tightness of connections also provide current indications of battery degradation. Most degraded battery conditions and stressors are detected by the practices outlined in IEEE-450 and Regulatory Guide 1.129, yet there are a few that have been discussed in this report that apparently are not covered. Table 13 is a tabulation listing degraded battery conditions and indicating those covered by the standards and guides. Items related to seismic vulnerability are not covered because a detection method other than actually testing selected cells has not been developed. Overcharging, while detrimental to a battery, is difficult to detect after the fact and appears not to be covered. Ripple in the output of a battery charge is detrimental to a battery, yet standards and guides applicable to both batteries or battery chargers do not appear to require periodic tests or measurements to detect excessive ripple.

A review of some plant procedures showed that weekly, monthly, quarterly, and refueling outage inspections similar to those in IEEE Std 450-1980 were being performed. However, this may not be true for all plants as indicated in IE Information Notice No. 85-74.[19]

> "Recent IE inspections of operating facilities indicate that widespread deficiencies may exist in the operation and maintenance of station batteries. These deficiencies are attributable to a variety of causes, including licensee error, inadequate knowledge of batteries by maintenance technicians and supervisors, and

Table 13. Battery conditions and stressors vs. IEEE STD 450 and Regulatory Guide 1.129

Battery Condition or Stressor	Covered by IEEE 450 and Regulatory Guide 1.129
External corrosion/contamination	Yes
Embrittled internal lead (seismic vulnerability)	Method not known
State of charge	Yes
Capacity of battery	Yes
Internal corrosion/flaking	Yes
Cracked containers	Yes
Faulty connections	Yes
Plate growth	Yes
Excessive battery charger ripple	Method is known but not required
High or low electrolyte level	Yes
High temperature of cells and environment	Yes
High or low float voltage	Yes
Loose or easily dislodged active material (seismic vulnerability)	Method not known
Overcharging	Method is known but not required
Prolonged under charging	Yes

inadequate procedural guidance. The results of these inspections suggest a general lack of appreciation amongst licensee personnel for proper maintenance and surveillance of station batteries. Although batteries contain no moving parts, considerable care and attention to detail is required to maintain them operable. Too often, licensees may be treating these vital engineered safety features (ESF) power supplies as 'passive' components and not providing them the necessary management and technical attention."

In conclusion, batteries maintained in accordance with recommended practices in Regulatory Guide 1.129 and IEEE Std 450-1980 should provide reliable service. However, as pointed out in NRC Information Notice No. 83-11, surveillance tests required by technical specifications will detect a degradation in a battery's ability to deliver its rated charge; they will not detect those degradations of a battery's structure making it vulnerable to seismic events. Furthermore, surveillance tests for identifying incipient seismic vulnerabilities of old batteries (other than seismic testing of selected cells) have not been identified. This presents a situation of potential concern because NRC Information Notice No. 83-11 also points out that most older batteries are not qualified to withstand a seismic event at their end-of-life condition.

> "...most batteries now used in nuclear power plants are not qualified to withstand a seismic event at their end-of-life condition. Even those batteries that are qualified in accordance with Regulatory Guide 1.100, 'Seismic Qualification of Electric Equipment for Nuclear Power,' are not necessarily brought to their end-of-life condition prior to seismic testing. Regulatory Guide 1.100 endorses IEEE Std. 344, 'Recommended Practices for Seismic Qualification of Class 1E Equipment for Nuclear Power Generating Stations.' At the end-of-life condition, the battery plates are more vulnerable because they are brittle. Also, material can slough off the plates, shorting out the battery, or reducing its capacity."[15]

Therefore, old batteries not seismically qualified at end-of-life conditions could fail during a seismic event.

8. PRELIMINARY IDENTIFICATION OF IMPROVED SURVEILLANCE

The previous section noted that the standard, commonly used, surveillance tests when properly implemented will detect degradation in a battery's ability to deliver its rated charge, but will not detect those degradations of a battery's structure that make it vulnerable to seismic events. Therefore, a preliminary investigation of surveillance tests with the potential to detect the types of degradation that will cause a battery to be vulnerable to seismic events has been performed. While the methods identified have not been proven, some are being actively studied by other researchers.

Six potential surveillance tests have been identified. These tests range from a precise measurement of cell voltage during discharge to the measurement of noise generated within cells during discharge. Cross-correlation techniques can be used to identify cells that are different from the average of those in the battery bank. This information may be useful in locating cells with internal degradation. The following is a brief discussion of each test:

<u>Precise measurement of cell voltage</u>—This test is a precise (within 1 mV) measurement of the dc voltage of each cell during a discharge of the battery bank. The voltages would be measured either continuously or often enough that a voltage versus time history could be obtained. Cells whose voltages are different would be identified as having an internal problem. The problems most likely to be observed are increased internal resistance due to corrosion/oxidation of the buses, grids, terminals, and active material. Also, corrosion at the interface between the active material and grids would cause the internal resistance to increase with a resultant decrease in cell voltage during discharge. Johnson Controls Company, a battery manufacturer, is presently working on this method and plan to soon have a battery bank system assembled and begin tests that will determine if the method is feasible for early detection of battery degradation. Variations of this method are also discussed in EPRI report NP-1558.[13]

<u>Measurement of internal resistance and capacitance</u>—Westinghouse R&D Center has prepared a report for Sandia National Laboratories reporting their investigation of the measurement of battery capacitance and resistance as a method of detecting degradation.[30] Capacitance is measured by applying a step charge current of about 1 amp to a fully charged cell while recording the cell's voltage response. Internal resistance is measured by interrupting a relatively small discharge current (about 10% of rated) and recording the instantaneous rise in cell voltage. The time constant is determined, measured capacitance is utilized, and resistance is then computed. A lower-than-expected capacitance is postulated to be indicative of a failure mode involving shedding of active material or plugging of pores in the active material. The resistance is a measure of the condition of the grids, the integrity of the busses, and the attachment of the active material to the grid. A statistical basis has not been developed yet to correlate changes in capacitance or resistance with specific degradations of the cell.

<u>Impedance measurement at different frequencies</u>—This method had been reported in several papers.[31,32] Impedance is measured during discharge over a range of frequencies from 10^{-2} to 10^{4} Hz. Values for resistance, capacitance, and inductance can be calculated from the impedance values and the equivalent circuit for the battery. These values are then utilized in a similar fashion as resistance and capacitance is in the previous discussion to assess battery degradation. While this method is similar to the previous method, it should provide more detailed information because impedance is measured at several frequencies and several states of charge. This method also allows inductance as well as resistance and capacitance to be calculated. Because more information is obtained, there will be more opportunity to detect a difference between a new battery and a degraded one. Problems related to introducing the ac voltage during a discharge test, as well as correlating differences in measured values with specific battery degradations, need to be investigated.

<u>Excite the battery with electrical white noise and measure frequency spectrum</u>—This method is an extension of the impedance measurement at various frequencies in that all frequencies are introduced simultaneously. No evidence has been found where this method had been applied to batteries, even though the technique has been used with other electrical systems with good success. The location and magnitude of peaks in the noise spectrum would be correlated, if possible, to battery-degradation mechanisms. Data would be taken on new batteries as well as batteries with known problems.

<u>Analysis of the natural electrical noise generated by the battery during discharge</u>—While similar to the previous technique, this method will analyze the noise naturally generated by a battery during discharge rather than measuring its response to noise that is introduced.

Again, no evidence has been found where this technique has been applied to batteries. The technique has been applied to other devices, e.g., RTDs, to determine parameters such as frequency response.[33] In addition, this method has been utilized as a condition-monitoring tool for electrical amplifiers, circuits, and transducers. All electrical devices generate some noise and this noise, in most cases, changes as the characteristics of the device change. The noise generated by the batteries would be analyzed to determine if changes in frequencies and magnitude could be correlated with changes in the internal degradation of the battery.

Correlation of visible degradation to seismic vulnerability—EPRI report NP-1558 has suggested a correlation between growth of the positive plates and useful life of a battery.[13] Because it is known that aging of batteries results in some visible effects, it is possible that a correlation may exist between seismic vulnerability and visible evidences of degradation. If successful, this would provide a simple, inexpensive method of detecting seismic vulnerability.

Some other methods were considered, such as chemical analysis, radiography, ultrasonics, and thermal inspection of the positive anode by infrared methods. Discussions with battery experts have led us to believe the information obtained by these methods would only indicate conditions of severe degradation. None of them would be able to detect incipient degradation soon enough to avoid utilizing a battery that is vulnerable to seismic events. Lead corrosion results in the formation of solid material that does not go into solution, which makes chemical analysis difficult. Visual examination of the batteries for cracked cases and solid particles is important as a routine maintenance practice, but cannot be depended upon to locate the problem of anode embrittlement early enough to ensure safety during a seismic event. Radiography, ultrasonic and thermal inspection of the grids, straps, and terminals within the battery case are difficult because the components are not readily accessible.

In conclusion, it appears that several methods could be developed to allow monitoring battery banks during rundown tests. None of the methods have been developed and all will require additional research to determine how effective they are at indicating specific problems and determining which, if any of them, can be implemented practically at a nuclear power plant. Some of these methods involving the measurement of resistance, capacitance, and voltage are being investigated by researchers and results may be reported by them. However, other methods such as the measurement of natural noise and the response to introduced white noise are not being investigated. While more complicated, these methods may provide more information concerning the degradation of a battery.

9. APPLICATION OF PROGRAM RESULTS TO STANDARDS AND GUIDES

Research conducted for this study has included a review of industry standards and NRC guides that are applicable to qualification, maintenance, testing, and replacement of batteries. As mentioned in the foregoing sections, thermally induced oxidation of the grids and top conductors that are made of a lead-calcium alloy causes older batteries to be potentially vulnerable to seismic events. Therefore, the primary issues are related to seismic qualification and early detection of internal degradations that can lead to seismic vulnerability.

Requirements for seismic qualification of batteries for nuclear power plants are covered by IEEE Standards such as 323-1983, "IEEE Standard for Qualifying Class 1E Equipment for Nuclear Power Generating Stations"; 344-1987, "IEEE Recommended Practices for Seismic Qualification of Class 1E Equipment for Nuclear Power Generating Stations" (latest version should be available July 1987); and 535-1986, "IEEE Standard for Qualification of Class 1E Lead Storage Batteries for Nuclear Power Generating Stations." NRC Regulatory Guide 1.100, "Seismic Qualification of Electric and Mechanical Equipment for Nuclear Power Plants" (the latest version will be available for public comment August 1987) also provides guidance for the qualification of batteries. IEEE Std 535 is the only standard of the above that specifically requires batteries to be aged to an anticipated qualified life before seismic qualification. However, the NRC staff plans to issue a Regulatory Guide, EE 006-5, "Qualification of Safety-Related Lead Storage Batteries for Nuclear Power Plants," for public comment by August 1987 which may include such a requirement. Seismic qualification should be performed with batteries that have been aged to end-of-qualified-life.

Requirements for maintenance, testing, and replacement of batteries are provided in IEEE Std 450-1980, "IEEE Recommended Practice for Maintenance, Testing, and Replacement of Large Lead Storage Batteries for Generating Stations and Substations," and Regulatory Guide 1.129, "Maintenance, Testing, and Replacement of Large Lead Storage Batteries for Nuclear Power Plants." As previously discussed, Regulatory Guide 1.129 endorses IEEE Std 450, with certain exceptions, and these documents outline adequate maintenance, testing, and replacement practices to provide reliable service. However, they will not detect those degradations of a battery's structure making it vulnerable to seismic events. If practical methods of detecting the internal degradations are developed, IEEE Std 450 should be modified to include the improved detection methods, or Regulatory Guide 1.129 could be modified by adding another section that would require the improved monitoring or testing.

10. CONCLUSIONS AND RECOMMENDATIONS

The objectives of this study were to identify significant stressors and aging mechanisms for batteries, identify field and test experience related to aging of batteries, evaluate the information on battery problems and failures contained in various data bases, and evaluate maintenance, testing, and monitoring methods. Several conclusions have been reached and are presented.

Batteries at nuclear plants are of the lead-acid storage type and are operated at "float" conditions (Floating is the term applied to the method of operation when the battery is continually connected to a battery charger to keep it in a fully charged condition by reason of the small amount of charging current that it receives.), with a battery charger, until a loss of all ac power requires the batteries to provide energy to supply critical functions. Redundant, independent batteries are installed to increase the likelihood that dc power will always be available. The batteries have a critical function and it is important that they be maintained at a level of high reliability to be available when needed.

The most common aging-related stress mechanism for batteries is thermally induced oxidation of the grids and top conductors that are made of a lead-calcium alloy. Lead experiences a 21% growth as it oxidizes to lead dioxide. This growth causes the plates (including grids) to swell, causing poor contact between the grid and the active material in the plate, and results in decreased capacity of the battery. In addition, plate growth may ultimately result in stressing the container and covers; causing cracks to develop in the container, and subsequent loss of electrolyte. The loss of electrolyte, if allowed to continue, could result in corroded battery supporting racks and decreased capacity due to low electrolyte level. High temperatures can result from overcharging, ac ripple from the battery charger, or from the environment. Ambient temperature increases from 77 to 95°F can reduce the life of a battery by 50% by accelerating oxidation and deterioration of battery components.

Operating experience combined with testing of naturally aged batteries indicates that cracking of the containers and oxidation (flaking) of the lead are significant problems. These failures have been the subject of NRC Information Notices and have been brought to the attention of the operators of nuclear power plants. Testing of naturally aged batteries has identified oxidation of the lead grids, straps, and terminals and deterioration of internal components as problems with batteries. These problems are common to old batteries near their end of life, and test results have shown that old batteries could then be vulnerable to seismic events. However, newer batteries qualified to the requirements of IEEE Std 535-1986, "IEEE Standard for Qualification of Class 1E Lead Storage Batteries for Nuclear Power Generating Stations,"[23] may be less vulnerable to seismic events because the IEEE Standard requires seismic qualification with batteries aged to end-of-life conditions.

Data from the NRC's Licensee Event Report (LER) system, the Institute for Power Reactor Operations' Nuclear Plant Reliability Data System (NPRDS), the Oak Ridge National Laboratory's In-Plant Reliability Data System (IPRDS), and The S. M. Stoller Corporation's Nuclear Power Experience (NPE) data base were analyzed to identify important failure causes and their relationship to aging. Analysis of data bases has resulted in the conclusion that events classified as representing a degraded or incipient-failure condition are the most commonly reported events. These events include low specific gravity, insufficient charge, cracked containers, corrosion, defective or weak cells, and faulty connections. Low specific gravity is the most common of these representing about 27% of the total battery-related events reported in LERs. Personnel errors in performing operations, maintenance, and testing also emerged as a significant factor representing about 21% of the total battery-related events reported in LERs. The possibility exists that personnel errors have contributed to some of the other reported failures such as low specific gravity and insufficient charge. Total battery failures peaked in the period of 6 to 11 years after the batteries were placed into service. These are age-related failures and are probably related to plate growth, deterioration of internal components, and cracked containers.

Batteries do not have moving parts and may not appear to be the kind of device that requires close attention to maintenance practices, yet considerable care and attention to detail is required to maintain them operable. We conclude that maintenance performed correctly leads to the long use of batteries and batteries maintained in accordance with recommended practices in Regulatory Guide 1.129 and IEEE Std 450-1980 should be expected to provide reliable service for their qualified life.

There is a need to develop improved surveillance and monitoring of nuclear power plant batteries. Surveillance tests required by technical specifications will detect degradation in a battery's ability to deliver its rated charge, but will not detect those degradations of a battery's structure that may make it vulnerable to even a mild seismic event. Furthermore, surveillance tests for identifying incipient seismic vulnerabilities of old batteries (other than seismic testing of selected cells) have not been identified. Because the useful electrical life of a battery is probably longer than its seismic-qualified life, old batteries not seismically qualified at end-of-life conditions may fail during a seismic event.

10.1 Recommendations for Phase II Study

Aging mechanisms, failure modes, and failure causes have been well studied and are understood and established. However, a need remains to identify advanced inspection, surveillance, and monitoring (IS&M) methods that can detect defects in the incipient stage that lead to seismic vulnerability. Because nuclear plants with batteries not qualified according to IEEE Std-535 appear to be common, a practical, cost-effective method to verify the ability of a battery to survive a seismic event is needed.

The Phase II study will utilize a combination of analysis and testing to identify the advanced IS&M methods that should be subjected to a testing program for further evaluation. Testing will include work with naturally aged batteries of varying design, age, and state of degradation. Batteries of three different models and four different ages are being obtained from the decommissioned Shippingport Atomic Power Station. One battery has been obtained from the Advanced Test Reactor at INEL and others will be obtained when available. Aged batteries from other nuclear plants will also be obtained and utilized in this study.

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ABSTRACT

This report presents the results of a study of aging effects on safety-related batteries in nuclear power plants. The purpose is to evaluate the aging effects caused by operation within a nuclear facility and to evaluate maintenance, testing, and monitoring practices with respect to their effectiveness in detecting and mitigating the effects of aging. The study follows the U.S. Nuclear Regulatory Commission's (NRC's) Nuclear Plant-Aging Research approach and investigates the materials used in battery construction, identifies stressors and aging mechanisms, presents operating and testing experience with aging effects, analyzes battery-failure events reported in various data bases, and evaluates recommended maintenance practices. Data bases that were analyzed included the NRC's Licensee Event Report system, the Institute for Nuclear Power Operations' Nuclear Plant Reliability Data System, the Oak Ridge National Laboratory's In-Plant Reliability Data System, and The S. M. Stoller Corporation's Nuclear Power Experience data base.

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